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Spatial and temporal influences of in-stream factors on the chemistry and epilithic biomasses of upland stream metal deposits

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Abstract

The density and composition of stream bed metal deposits are affected by physical, chemical and biological processes. In this paper we investigate the importance of these processes and their relation to algal and non-photosynthetic detrital (NPD) biomass in a set of upland streams in Northern Ireland. Deposit density and Fe, Mn, Al and P concentrations varied with stream pH across sites but not seasonally. No effects of stream bed erosion or photoreduction were detected on deposit densities. Seasonal variation in stream water metal concentrations was correlated with rainfall. NPD biomass was a significant predictor of both spatial and seasonal variation in deposit concentrations. There were strong, non-linear, relations between NPD biomass and deposit metal concentrations, with Fe and Mn becoming relatively more important and algal biomass declining above threshold deposit/NPD densities. The results suggest that NPD biomass influences deposit density and reduces the biomass of photosynthetic autotrophs above a threshold deposit density.

Keywords

Iron deposits · Epilithic algae · pH · Dissolved oxygen · Rainfall · Photoreduction

Introduction

Deposits of iron oxide in surface waters have been documented globally (Niyogi et al. 1999; Prange 2007; Neal et al. 2008) and are frequently reported in post-industrial landscapes impacted by acid mine drainage (Younger 2001; Kimball et al. 2002; Mayes et al. 2008). Stream metal deposits are also found in non-industrial, often upland, catchments with limited anthropogenic activity. In impacted areas, metal rich precipitates are ubiquitous and envelop benthic habitats. Smothering by flocculent precipitates reduces light penetration and oxygen circulation at the substrate level within streams (Mayes et al. 2008), which in turn has negative impacts for benthic primary producers and limits nutrient transfer between trophic levels. The deposits have potentially harmful effects for algae, invertebrates and fish (Vuori 1995; Jarvis and Younger 1997).

A variety of physical, chemical and biological factors determine the quantity of metal-rich deposits found in some upland streams through redox processes. An extensive literature documents the mobilisation of soluble ferrous iron (Fe) under acidic, deoxygenated conditions, as found in water-logged peaty soils, and the precipitation of the ferric form in less acidic, more oxygenated, surface waters (Crerar et al. 1979; McKnight and Feder 1984; Abesser et al. 2006; Prange 2007). pH, oxygen and temperature are highlighted as important environmental factors controlling the speciation of Fe; the influence of pH on oxidation rate is strongest under circumneutral conditions (Morgan and Lahav 2007). Photoreduction (Madsen et al. 1986; McKnight et al. 1988; McKnight et al. 2001) and the erosion of deposits by stream flow (Abesser et al. 2006) reduce the amount of deposit material diurnally and seasonally. Manganese (Mn) behaves similarly to Fe (Rowland et al. 2012), although it precipitates at a higher oxygen concentration (Stumm and Morgan 1996) and its oxide minerals can scavenge substantial amounts of many metals, including Fe from the environment (Tebo et al. 2004).

Stream bed organic matter can be divided into phototrophic (algal) and non-photosynthetic detrital (NPD) components: NPD potentially consists of bacteria, fungi, extracellular biofilms and detritus of terrestrial or aquatic origin (Ledger and Hildrew 1998; Carr et al. 2005). Bacteria are the most common agents of Fe deposition, although algae and fungi can precipitate metals under some circumstances (Ghiorse 1984; Trouwborst et al. 2007). Metal-oxidising bacteria are significant biogenic agents (Crerar et al. 1979; Konhauser 1998; Tebo et al. 2004; Emerson et al. 2010) and cause/enhance the deposition of metals in streams as (hydr)oxides. For example, *Leptothrix* and *Gallionella*, common bacterial genera inhabiting Fe- and Mn-rich freshwater environments (Johnson et al. 2012), occur at circumneutral pH and are characterised by the extensive production of oxide encrusted sheaths and stalks (Ghiorse 1984; Sheldon and Wellnitz 1998). In addition, aluminium (Al), Fe and Mn compounds precipitate/complex with phosphorus (P), with potential nutrient supply effects for biofilm organisms.

Catchment (soil type and geology) and in-stream (pH and dissolved oxygen (DO)) variables influence stream water metal concentrations in upland streams in Northern Ireland (Macintosh and Griffiths 2013). In this study, we investigate the factors that affect deposit concentrations and algal and NPD biomasses both spatially and temporally. The purpose of this process-level study was to investigate:

(1) If stream water chemistry, and in particular pH and DO, affects metal deposit concentrations by altering metal solubility (Hem 1972; McKnight and Bencala 1990; Prange 2007). Deposit concentrations should increase with stream pH and DO.

(2) Whether stream bed erosion and/or photoreduction affect deposit density. Catchment hydrology and the rate of flushing are known to affect stream water metal loading and deposit metal concentrations (Abesser et al. 2006). If so, deposit density should vary seasonally, being negatively correlated with rainfall and day length.

(3) The relative importance of epilithic algae and NPD in determining deposit composition and whether biotic or abiotic processes affect stream bed deposit concentrations. Photo- and litho-trophic activity may control stream deposit metal concentrations (Konhauser 1998; Emerson et al. 2010). The relative contributions of pH and deposit organic matter to predicting deposit inorganic matter concentrations should help to identify the roles of chemical and biological processes, respectively. This hypothesis was tested by determining the contributions of in-stream factors (pH, DO, algal and NPD biomasses) and rainfall to predicting deposit density and composition.

Materials and methods

Study area

Macintosh and Griffiths (2013) have described the study sites adopted in a survey of 52 sites located in two geologically distinct upland areas of Northern Ireland. Sites lack anthropogenic interference and are not impacted by mining activities. The current paper uses data collected in April 2007 from 32 of these sites, located in the Sperrin Mountains, and from eight of these sites in two adjacent catchments, sampled approximately monthly on 12 occasions between November 2007 and September 2008. Sites were selected across a range of deposit metal concentrations. All streams were located on open moorland, had well-oxygenated water and stony substrata: no aquatic macrophytes were observed. Streamflow tended to be ‘flashy’, with rapid fluctuations between high and low flow discharge. Medians and ranges of physical, chemical and biotic variables across sites are summarised in Table 1: with the exception of oxygen saturation levels the variables vary by 1-3 orders of magnitude across sites. The benthic chlorophyll *a* and phosphorus concentrations indicate that these streams are oligotrophic (Dodds et al. 1998).

Sampling and laboratory analysis

Water chemistry procedures for Fe, Mn and Al are detailed in Macintosh and Griffiths (2013). Stream water total phosphorus (P) concentrations were determined by spectrometry using the molybdate-antimony method (Murphy and Riley 1958, 1962). Stream water was analysed, *in situ*, for DO, temperature, conductivity and pH. A HACH HQ 10 portable meter with LDO probe was used to measure DO (% saturation) and temperature (°C), while a HACH sensION™156 portable meter was used to measure conductivity (µS cm^{-1}) and pH. Probes were calibrated prior to sampling in accordance with HACH operation manuals.

On each sampling occasion, seven stream bed stones were randomly removed from each site and bagged individually for analysis of deposit composition and epilithic chlorophyll *a* concentration. Deposit material on the upper stone surface was removed by spatula, brush and rinsing with Millipore Milli-Q grade water. Depending on density, the material from two to three stones was amalgamated and dried at 105°C until there was no further weight loss. Inorganic matter (IM) was determined after ashing deposit samples for 1 hour in a muffle furnace at 550°C, and organic matter content (OM) estimated as the loss-on-ignition (Lamberti and Resh 1985). Deposit density was calculated as the dry mass of material per unit surface area, the latter determined by covering the exposed stone surface with aluminium foil which was then weighed. Surface area of the stones collected varied five-fold, from 49-259 cm^2, but surface area did not affect deposit density estimates (two-way ANOVA with site and area as variables; $F_{1,196} = 1.22$, $P>0.2$): similar results were obtained for each metal. IM was strongly correlated with total deposit density ($r = 0.99$, $n = 32$, $P<0.001$): it comprised on average 68% of deposit (range 47-92%). After sequential digestion with concentrated hydrofluoric, nitric, and perchloric acids, deposit chemistry was measured by spectrometry as described for water chemistry by Macintosh and Griffiths (2013).

Epilithic algal chlorophyll *a* concentrations on four stones were determined following the procedure of Marker et al. (1980), after cold extraction in the dark at 4°C. Optimum stone sampling effort for chlorophyll *a* concentration was determined by bootstrapping, using a Mersenne-Twister random number generator, to randomly resample 1000 observations with replacement, from an original sample of 10 (Quinn and Keogh 2002). Published data on ash free dry weight (AFDW) and chlorophyll *a* concentrations (Chla) were compiled and the autotrophic index (AFDW/Chla), an indicator of the relative importance of phototrophic and lithotrophic biomass components, was calculated. Indices less than 200 were taken as indicative of sites where photosynthesis dominated primary production (Rice et al. 2012), higher values indicating predominantly lithotrophic production. Using the equation derived from published data (Clark et al. 1979; Weitzel et al. 1979; Biggs 1996; Carpenter 2003) for non-Fe deposit sites with an autotrophic index <200 ($\log AFDW = 2.016 + 1.043 \pm 0.026 \log Chla$, $r^2 = 0.98$, $n = 37$), we estimated the AFDW attributable to photosynthetic organisms (algal biomass) from measured deposit chlorophyll *a* concentrations. The difference between algal biomass and the corresponding OM values was used as an estimate of 'non-photosynthetic detrital' (NPD) biomass. NPD biomass includes extracellular and allochthonous organic matter, dead algae, bacteria and fungi (Ledger and Hildrew 1998; Carr et al. 2005).

Dissolved organic carbon (DOC, data supplied from the Geological Survey of Northern Ireland Tellus Project) is an important energy/nutrient source for lithotrophs (Bott et al. 1984; Tranvik 1988), and should be correlated with the NPD biomass estimates: it was, but not with algal biomass ($r = 0.42$, $n = 30$, $P<0.05$; $r = -0.11$, $n = 30$, $P>0.5$, respectively). The Tellus Project data were collected at a different spatial scale and on different dates from our samples, so as a check on comparability we calculated correlations between variables measured in common (conductivity, pH, Fe, Mn, Al): the correlation for Al was not significant (r = 0.20) but those for the other variables were (r = 0.75 – 0.86, n = 30, P<0.001).

If photoreduction has a significant seasonal effect on deposit concentration, a negative correlation between day length and concentration would be expected. Day length for the sample dates was estimated for the mean latitude and longitude of the sites (using http://aa.usno.navy.mil/data/docs/RS_OneYear.html), while mean values across sites were used for all deposit variables. The low angle of the sun in the winter results in greater reflection and less light penetration, and consequently day length overestimates photic effects.

To assess the role of flushing from the catchment daily rainfall data for October 2007 to October 2008 was obtained from the Meteorological Office weather station at Banagher, Caugh Hill, on the edge of the Sperrin Mountains, the closest station (10-12 km north) to the eight seasonal study sites.

Statistical analysis

The effect of rainfall on deposit concentrations was determined by calculating the cumulative rainfall in the 3, 7, 14 and 28 day periods prior to sampling. To summarise rainfall effects, the numbers of significant correlations were expressed as fractions of possible correlations.

All variables, except temperature, DO and pH, were $\log_{10}$ transformed to normalise the data. In the majority of tests, a 5% significance level was used; but significance levels between rainfall and metal concentrations in stream water were increased to 10% to reduce the risk of type 2 error with the low-resolution rainfall data. To test for non-linearity, the fits of piecewise (Toms and Lesperance 2003) and linear regression models were compared using AIC_c. Non-linear lines were fitted to the data using locally weighted scatterplot smoothers (lowess).

Results and Discussion

Effect of stream water chemistry

Stream water in the Sperrin Mountains was usually saturated with oxygen (Table 1: seasonal data, median DO 105%, range 94 –117%), whereas pH was more variable (median 6.7, range 4.6 – 8.7) (mean coefficients of variation ± s.e. for DO and pH 0.057±0.004; 0.115±0.008, t = 6.19, P<0.001) and hence pH would be expected to be more important in determining metal deposition variation. Across all sites, deposit density and total Fe, Mn, Al and P deposit concentrations were negatively correlated with pH, but only Fe showed a correlation with DO (pH r = -0.44 – -0.53, P<0.05; DO Fe r = -0.41, n = 25, P<0.05).

There were consistent temporal trends in stream water chemistry (results not shown) and in deposit concentrations across sites (Kendall coefficient of concordance: deposit χ^2 = 56.7, P<0.001; Fe_d χ^2 = 62.2, P<0.001; Mn_d χ^2 = 55.7, P<0.001; Al_d χ^2 = 32.7, P<0.001; P_d χ^2 = 37.3, P<0.001), suggesting that this variation is driven by seasonal factors.

pH and DO are recognised in the literature as major determinants of metal solubility (Hem 1972; McKnight and Bencala 1990; Prange 2007) and hence potentially important predictors of chemical metal precipitation within stream systems. The lower variability in DO may relate to the turbulent dynamics of the upland stream sites, which are generally fast flowing and subsequently well oxygenated. However, the negative correlations between the deposits and pH and DO are contrary to expectation if deposition is controlled by chemical processes and stream water concentrations.

Erosion and photoreduction

There was little evidence of a stream bed erosion effect; only three of 32 possible correlations (8 sites x 4 rainfall periods) between rainfall and deposit density were significant and only two were negative. Mean deposit Fe, OM and NPD biomass concentrations increased with day length, contrary to expectation if there was a strong photoreduction effect (r = 0.78, 0.69, 0.71, n = 9, P<0.05, respectively): there was no temperature effect on any of the deposit variable concentrations.

Failure to detect erosion and photoreduction effects on stream bed deposits is probably more a reflection of sampling resolution than the absence of such effects. For example, on several occasions the majority of tiles secured to the stream bed to measure deposit accrual rates were lost, indicative of strong erosional episodes. Nevertheless, the short-term (<7 day) correlations between rainfall and deposit concentration are positive, inconsistent with an erosion effect. Fe and DOC surface water concentrations are positively correlated (Molot and Dillon 2003; Neal et al. 2008; Macintosh and Griffiths 2013), because both are derived largely from the catchment (Vuori 1995). However, Fe^{3+} forms complexes with dissolved OM, which increases the likelihood of photoreduction. Photoreduction occurs with a diurnal cycle (McKnight et al. 1988; McKnight et al. 2001), so the positive seasonal correlation with day length which we report must be due to some other process.

Catchment flushing

Over the year, the greatest number of significant correlations was between stream water metal (Fe, Mn, Al) concentrations and total rainfall in the previous 8-14 days (8 sites x 3 variables x 4 rainfall periods = 96 possible correlations: 1-3 days, 6/96 significant at P<0.10; 4-7 days, 5/96; 8-14 days, 17/96; 15-28 days, 1/96). It should be noted that the overall number of correlations is similar to that expected by chance: higher resolution data are necessary to confirm a rainfall effect. All significant correlations for rainfall periods up to 7 days were positive, consistent with a short-term flushing effect from the soil, but for longer periods all correlations were negative. All Fe correlations (8 sites) were negative, but positive and negative correlations occurred for Mn (6/14 positive) and Al (5/7 positive).

Precipitation and translocation of water through various hydrological pathways is responsible for nutrient and metal transport into lotic systems (Carlyle and Hill 2001; Abesser et al. 2006). Hence, low rainfall can result in high soil metal concentrations, while persistent heavy rainfall following a dry period can flush metals from soils into streams, but with concentrations declining as material is removed. Abesser et al. (2006) identified soilwater and groundwater sources for Fe and Mn in three upland catchments. They concluded that metals were flushed from the soil during storm events and that the lower concentration groundwater source became more important as the soil reservoir was depleted. Fe, Mn and Al water concentrations were shown to respond positively and rapidly to increases in streamflow. Such relationships are detectable with *in-situ* monitoring equipment for the collection of site-specific, hydrometric and water chemistry data: high-resolution data were not collected as part of this study. However, the short-term (< 7 days) positive and the longer-term (>7 days) negative correlations observed in our data could be generated by a similar relationship, although the stream water metal responses to rainfall appear to be much slower than those observed by Abesser et al. (2006).

Deposit composition

Deposit IM concentrations were predicted by deposit OM concentrations but not by pH or DO (Table 2a) and NPD biomass was a stronger predictor than algal biomass (Table 2b). Deposits tended to be dominated by either algal or NPD biomass (Fig. 1): none of the in-stream variables were distributed bimodally. Algal biomass across sites was not correlated with any of the other deposit variables, which were strongly correlated with each other (r = 0.56 – 0.90, median 0.76, n = 15) and with the first principal component (PCA) axis (Table 3): Al showed an intermediate association with the PCA axes. The first two factors accounted for 85% of the variation in deposit composition. There were marked seasonal changes in algal biomass but much less change in NPD biomass (Fig. 2).

Across the 32 sites, NPD biomass had stronger effects on deposit metal concentrations than algal biomass or stream water concentrations (Table 4a). Similarly, across sample dates, NPD biomass was a significant predictor for all determinants, whereas pH, 7 day rainfall and algal biomass were only occasionally significant (Table 4b).

OM content increased linearly with overall deposit density, which is to be expected since it comprised an average of 32% (range 8-53%) of the deposit. However, metal and P concentrations across the eight intensively studied sites exhibited non-linear relations with NPD biomass (Table 5, Fig. 3), OM and deposit density: concentrations showed small (Fe, P) or no increases (Mn, Al) up to deposit densities of 4-8 mg cm^{-2} before increasing more rapidly. Above the breakpoint the slope for Fe, Mn and P was greater than 1.0, indicating an increasing proportion of these substances in the deposit, whereas the proportion of Al declined.

Algal biomass showed weak but significant, dome-shaped, relationships with NPD biomass, OM and deposit density (quadratic r = 0.29, n = 80, P<0.05; r = 0.33, n = 80, P=0.01; r = 0.29, n = 80, P<0.05, respectively) i.e. algal biomass was lower in the most OM rich and deposit dense sites.

DO and pH were not significant predictors of variation in deposit metal concentrations once deposit biomass was included in the analyses (Tables 2 & 4), with NPD biomass having the statistically dominant effect. Both Fe and Mn can be precipitated by purely chemical processes, but Fe and Mn-oxidising bacteria are also frequently involved (Ehrlich and Newman 2009). The majority of Mn oxides are biogenic in origin (Tebo et al. 2004), while Emerson et al. (2010) note that bacteria are responsible for about half the Fe oxidised in freshwaters. Bacterial growth rates surpass those of epilithic algae and bacteria are considered superior competitors for inorganic nutrients and space (Rier and Stevenson 2002). The strong relationships between NPD biomass and Fe and Mn concentrations in the stream bed deposits, but not with stream water concentrations, support a biogenic effect. While phototrophic activity can drive Fe deposition under some circumstances (Trouwborst et al. 2007), it seems unlikely to do so in the oligotrophic streams studied.

The bimodal distribution of epilithic algal biomass as a percentage of OM and the decline in algal biomass at high NPD biomass are both consistent with increasing metal deposition and a competitive interaction with lithotrophs. NPD biomass potentially includes extracellular and allochthonous organic matter (Ledger and Hildrew 1998; Carr et al. 2005), dead algae, bacteria, fungi and bacterial sheaths, in addition to live bacteria and fungi. There was little visible coarse particulate organic matter (CPOM) or fungal material in the samples (Macintosh K.A. unpublished data), but empty *Leptothrix ochracea* sheaths and the stalks of *Gallionella ferruginea* were observed under a microscope. Due to the scarcity of CPOM and fungi, we tentatively conclude that bacteria and/or their sheaths could be responsible for metal deposition. Elevated concentrations of Fe and Mn in streams promote the transition from photosynthetic production to lithotrophy, through the suppression of algal activity and/or increased bacterial populations (Sheldon and Skelly 1990; Rier and Stevenson 2002).

Conclusions

In this paper we investigated the spatial and temporal influences exerted by in-stream factors on the chemistry and epilithic biomasses of upland stream metal deposits. Deposit density and concentrations of Fe, Mn, Al and P varied with NPD biomass. Seasonal variation in stream water metal concentrations was correlated with rainfall; however, no effects of stream bed erosion or photoreduction were detected on deposit densities. Strong, non-linear relations exist between NPD biomass and deposit metal concentrations, with Fe and Mn becoming relatively more important and algal biomass declining above threshold deposit/NPD densities.

Our results, while only correlative, suggest the potential importance of microbial lithotrophic activity in determining seasonal patterns in deposit chemistry in naturally occurring, iron-impacted stream systems. A potentially important relationship exists between non-photosynthetic detrital biomass and the deposition of iron-oxides. This finding supports the growing body of literature that proposes a link between organic carbon and iron deposition (Weiss et al. 2003; Roden et al. 2012). Further investigation into the specific microbial mat ecology of such naturally occurring iron deposits is necessary to quantify the importance of bacterial oxidation of Fe and Mn.

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Table 1 Medians and ranges of physical, chemical and biotic variables across the 32 study sites.

Variable	Median	Range
Water		
pH	7.5	6.6-7.8
DO (%)	100.8	92.2-111.3
Fe (mg L^{-1})	1.37	0.01-6.28
Mn (mg L^{-1})	0.39	0.02-1.59
Al (mg L^{-1})	0.08	0.02-0.94
P (mg L^{-1})	0.01	0.005-0.039
Deposit		
Density (g m^{-2})	65.0	5.7-347.0
Fe (g m^{-2})	5.7	0.2-52.5
Mn (g m^{-2})	0.5	0.03-14.5
Al (g m^{-2})	1.0	0.2-8.9
P (g m^{-2})	0.1	0.01-0.8
IOM (g m^{-2})	44.8	4.1-280.3
OM (g m^{-2})	16.0	1.6-83.2
Algal biomass (g m^{-2})	2.2	0.1-45.2
NPD biomass (g m^{-2})	10.2	1.0-82.6
Autotrophic index	1319	42-20518

Table 2 Standardised multiple linear regression coefficients, showing inorganic matter concentration in the deposit varies (a) with deposit organic matter content (R^2 = 0.76) and (b) with NPD biomass (R^2 = 0.73).

(a)

Variable	Std Coeff	*t*
pH	0.011±0.040	0.29
DO	-0.009±0.037	0.24
Organic matter	0.865±0.102	8.51***

(b)

Variable	Std Coeff	*t*
Algal biomass	0.129±0.067	1.92
NPD biomass	0.750±0.098	7.66***

P<0.05*, *P* <0.01**, *P* <0.001***

Table 3 PCA component loadings on the first two axes for stone deposit ($_d$) variables. Significant loadings (P<0.05) are shown in bold.

	Factor 1	Factor 2
Fe_d	**0.943**	0.128
Mn_d	**0.843**	0.255
Al_d	**0.745**	**-0.437**
P_d	**0.898**	0.149
Inorganic matter	**0.941**	-0.208
Algal biomass	0.037	**-0.964**
NPD biomass	**0.900**	0.096
% variance	66.6	18.2

Table 4 Summary of multiple linear regressions, showing standardised coefficients of variables tested as predictors of deposit and metal concentrations (a) across sites and (b) across sample dates.

(a)

	Deposit		Fe		Mn		Al		P	
	Std Coeff	*t*	Std Coeff	*t*	Std Coeff	*t*	Std Coeff	*t*	Std Coeff	*t*
Water concentration			0.42	3.40**	0.39	1.70	-0.16	0.89	0.12	0.72
Algal biomass	0.07	2.00*	-0.09	1.13	-0.20	1.37	0.52	2.54**	-0.03	0.26
NPD biomass	0.68	2.90**	0.58	4.73***	0.36	1.55	0.92	4.29***	0.73	4.46**
R^2	0.46		0.88		0.53		0.47		0.66	

(b)

	Deposit		Fe		Mn		Al		P	
	Std Coeff	*t*	Std Coeff	*t*	Std Coeff	*t*	Std Coeff	*t*	Std Coeff	*t*
Water concentration			-0.01	0.29	-0.11	1.30	-0.03	0.70	0.05	1.63
DO	0.01	0.38	0.00	0.02	-0.01	0.07	0.03	0.69	0.01	0.13
pH	0.01	1.73	-0.02	0.50	0.17	1.82	0.02	0.33	-0.14	3.15**
Rain (28d)	0.00	0.07	-0.01	0.37	-0.20	1.90	0.00	0.07	0.05	0.94
Rain (7d)	0.04	1.39	0.03	0.87	0.21	2.19*	0.06	1.16	-0.07	1.52
Algal biomass	0.06	2.61*	-0.03	1.13	-0.23	2.71**	0.06	1.25	0.01	0.03
NPD biomass	0.47	23.75***	0.62	23.43***	0.55	8.69***	0.18	4.95***	0.35	11.56***
R^2	0.90		0.93		0.57		0.30		0.71	

P<0.05*, *P* <0.01**, *P* <0.001***

Table 5 Summary of linear and piecewise regression analyses (all values are $\log_{10}$ mg cm^{-2}, NPD biomass as the independent variable, n = 75) of the data shown in figure 3. ΔAICc was used to compare the fit of linear and piecewise models. The statistics of the best fitting models are shown: breakpoint is the NPD biomass at which the line changes slope and b1 and b2 are the slopes below and above the breakpoint. Significant slope values (b = 0) are shown in bold.

Deposit variable	a	b1	b2±se	breakpoint	R^2	ΔAICc	$t_{b2=1}$	$P_{b2=1}$
Fe	-0.315	**0.636**	**1.138**±0.055	-0.117	0.94	30.84	2.51	<0.05
Mn	-1.092	0.022	**1.225**±0.213	0.036	0.71	5.69	1.06	
Al	-0.791	-0.113	**0.668**±0.159	0.325	0.87	13.19	2.09	<0.05
P	-2.011	**0.363**	**1.583**±0.251	0.801	0.98	20.86	2.32	<0.05

Figure captions

Fig. 1 The percentage contribution of algae to organic matter in deposits across sites is bimodally distributed.

Fig. 2 Seasonal changes in mean (±1 s.e.) algal (triangles) and NPD (circles) biomass (mg cm^{-2}) across sites, between November 2007 and September 2008.

Fig. 3 Across the seasonally studied sites, Fe (circles), Mn (crosses), Al (diamonds) and P (triangles) deposit densities change as NPD biomass increases. Lowess smoothed lines (tension 0.6) are fitted to the data.

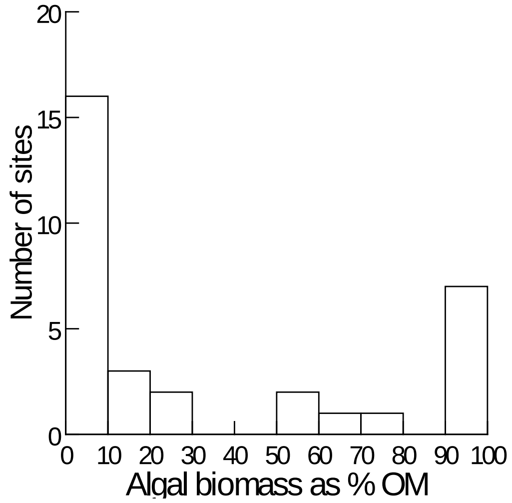
Number of sites
0
5
10
15
20
0 10 20 30 40 50 60 70 80 90 100
Algal biomass as % OM

Fig. 1

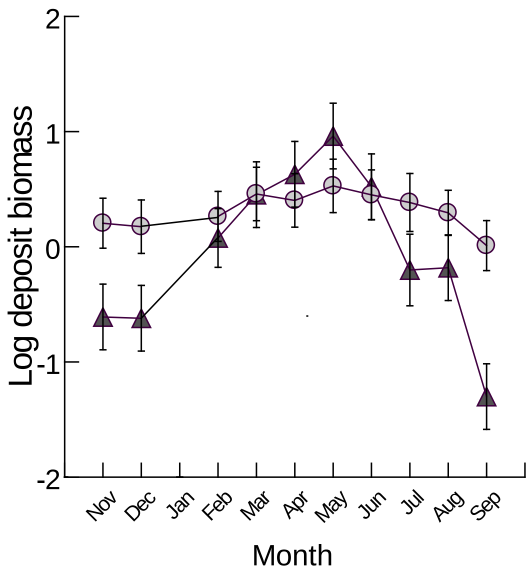
2
1
0
-1
-2
Log deposit biomass
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Month

Fig. 2

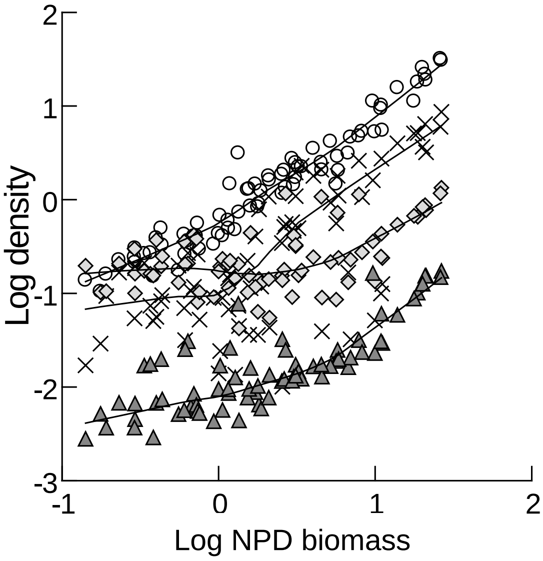

Fig. 3